Supporting Information

Tetraethylammonium hydroxide (35 wt.%) (TEAOH), aluminum powder, fumed silica, zinc acetate dehydrate, Ludox© HS-40, pure silica MCM-41, and tetraethylammonium fluoride were purchased from Aldrich. Lithium hydroxide and tetraethylortho silicate (TEOS) were purchased from Fisher. Phenethyltrimethoxy silane (PETMS) was purchased from Gelest.

Nanocrystalline aluminosilicate (SiO_2/Al_2O_3 = x) zeolite beta was synthesized by a previously published procedure[1,2]. The final molar gel composition was 1.0 Al_2O_3:(*v**(1-*w*)) SiO_2:(*v***w*) PETMS:(0.26**v*+1) TEAOH:15**v* H_2O where *v* ranged from 50 to 1000, and w was 0 or 0.025 (2.5 % Si coming from the PETMS). Half of the TEAOH was combined with the desired amount of aluminum powder. The other half of the TEAOH was combined with water and fumed silica. Both mixtures were stirred until all aluminum had dissolved. The mixtures were then combined and stirred with a Teflon bar for one hour. PETMS was then added, if desired, and the sample was stirred for one more hour. The gel was then loaded into Teflon lined stainless steel autoclaves (Parr). Typical crystallization parameters were 7 days at 140 °C with rotation at ~60 RPM. Crystallization products were collected by centrifugation, 1 hours at 50,000 g., and dried at 100 °C. PE containing samples (PE-BEA-x) were treated with 96 wt.% H_2SO_4 at 80 °C for 24 hours to remove the $TEA^+(OH^-)$. The extraction was repeated 2-3 times to ensure maximum removal of the structure directing agent (SDA). Following extraction, samples were dried at 110 °C under a rough vacuum and subsequently sulfonated by treatment with oleum for 12 hours at room temperature. See Figure S1. Oleum treated samples (S-PE-BEA-x) were quenched by addition to 500 mL of cold water followed by filtration and washing with at least 2 L of water. Samples were further washed by repeated sonication/centrifugation while monitoring the effluent pH. Samples were washed until the effluent pH was the same as the washing water (and until measured conductivity values did not change with subsequent washing). Non PE containing samples (BEA-x) were calcined at 550 °C in flowing air. The temperature was increased to 550 °C over 6 hours and then held at 550 °C for another 6 hours. Ammonium exchange was accomplished by contacting the samples with 1 M NH_4Cl at 90 °C for 24 hours. The supernatant was poured off and fresh solution was added 2-3 times to ensure maximum exchange. Samples were then collected by filtration, washed and dried at 100 °C. Thermal desorption of ammonia at 400 °C was used to produce proton exchanged samples.

Micrometer-sized pure silica beta (PS-BEA) was synthesized by dissolving the required amount of tetraethylammonium fluoride in water (6.25g TEAF/7.75 g water). Tetraethylorthosilicate and PETMS were then added and the initially 2-phase mixture was aggressively stirred for 12-24 hours. The resulting creamy white slurry was rotovaped to remove ethanol and excess water, and the appropriate amount of water was

added back to the solution so that the final gel had a molar ratio of 0.55 TEAF:*x* PETMS:(1-*x*) SiO_2 (TEOS): 7.25 H_2O. The thick gel was loaded into Teflon lined stainless steel autoclaves and heated, with rotation, in a convection oven to 140 °C. Crystallization times for non functionalized material was 5 days while phenethyl functionalized samples required 27 days[3,4]. Crystallization products were collected by filtration, washed with water and acetone, and dried at 100 °C. Aforementioned calcinations procedures were used to remove the SDA from non functionalized materials. PE functionalized materials were contacted with 1:1 (by volume) glacial acetic acid:water mixtures for 24 hours at 80 °C to remove occluded SDA molecules. The extraction procedure was repeated 2-3 times to ensure maximum removal of the SDA. The same procedure as described above was used to sulfonate the phenethyl groups.

CIT-6[5,6] and PE-CIT-6 were synthesized by dissolving lithium hydroxide and tetraethylammonium hydroxide in water. Zinc acetate dihydrate was then added and the mixture was stirred until all solids were dissolved. Dupont HS-40 silica was then added and the mixture was stirred for 1 hour. PTEMS was then added and the mixture was stirred for another two hours. If no PETMS was added, the mixture was stirred for a total of two hours. The final gel composition was 0.05 LiOH:0.65 TEAOH:0.03 $Zn(CH_3COOH)_2 \cdot 2H_2O$:*y* PETMS:(1-*y*) SiO_2:30 H_2O, where *y* was 0 or 0.025. The resulting clear liquid was loaded into Teflon lined stainless steel autoclaves and heated statically for 165 hours at 140 °C in a convection oven. Crystallization products were collected by filtration, washed with water and acetone, and dried at 100 °C. Non PE functionalized samples were calcined according to the aforementioned procedure. PE containing samples were extracted 2-3 times using the aforementioned acetic acid:water method. PE groups were sulfonated per the previously described method.

Phenethyl groups were grafted onto the surface of MCM-41 using the following procedure. MCM-41 (1 g) was dispersed into 100 mL toluene for 10 minutes with stirring. 4 mmol PETMS/g MCM-41 was added by syringe to the dispersion and the mixture was allowed to stir for 1 hour before the temperature of the oil bath was increased to 110 °C, causing the toluene to reflux. The grafting procedure was allowed to proceed for 24 hours. Grafted samples were collected by filtration and subsequently washed with 1 L of toluene (2 x 500 mL), 1 L of ethanol (2 x 500 mL), and 2 L of acetone (4 x 500 mL). The aforementioned oleum procedure was used to sulfonate the PE groups.

^{29}Si CPMAS and ^{13}C CPMAS NMR spectra were recorded using a Brucker Avance 200 MHz (^{1}H) spectrometer and 7mm zirconia rotors. TGA data were collected using a Netzsch STA 449 C and Pt/Rh samples dishes. Powder x-ray diffraction patterns were obtained using a Scintag XDS 2000 with Cu k-a radiation.

Our proton conductivity apparatus consisted of a Delrin© sample holder with 4 mm diameter sample wells. Samples were compressed, after hydration with water,

between two 4 mm diameter Pt cylinders using a torque screwdriver. A digital micrometer was connected to, but electrically isolated from, the Pt cylinders for *in-situ* sample thickness measurement. Samples were compressed to 80 in-oz (~500 psi) and held at this pressure for the duration of the measurement. A schematic of the sample holder is shown in Figure S1. The conductivity is calculated from the low frequency intersection of the semi-circular arc with the real axis. At lower frequencies, a straight line routinely attributed to electrode polarization is observed (not shown).

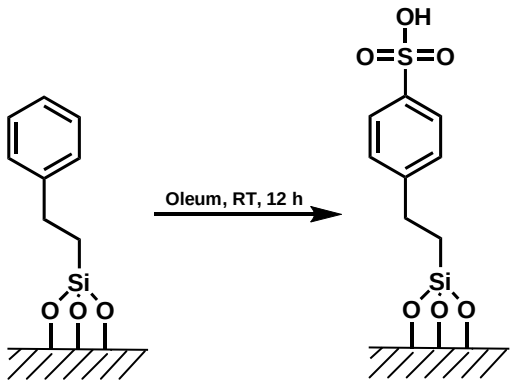

Figure S1. PETMS was incorporated into the pores of zeolite beta, or grafted onto the pore walls of MCM-41, and sulfonated using oleum

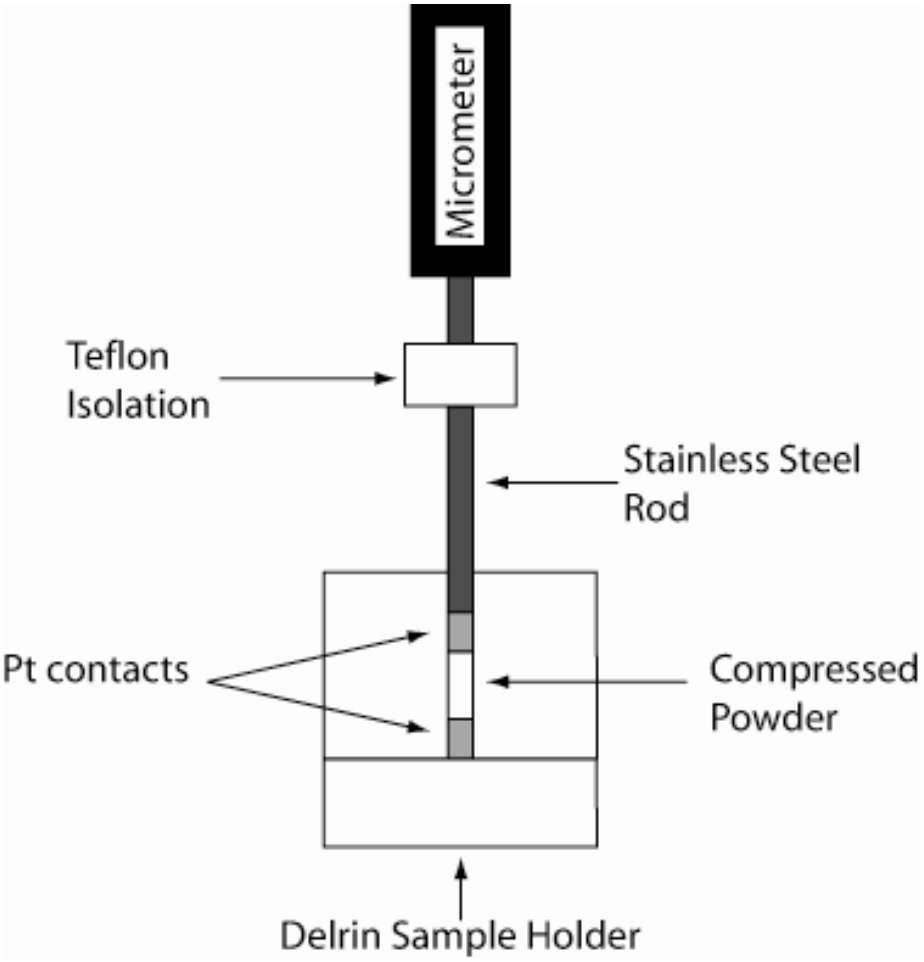

Figure S2. Sample holder used for proton conductivity measurements. Powder samples were loaded on top of the bottom Pt contact and allowed to equilibrate with water. The top contact was then inserted and the sample was compressed by applying torque to the micrometer with a torque screwdriver. An aluminum frame (not shown) held the structure in place, and the micrometer was zeroed before loading each sample.

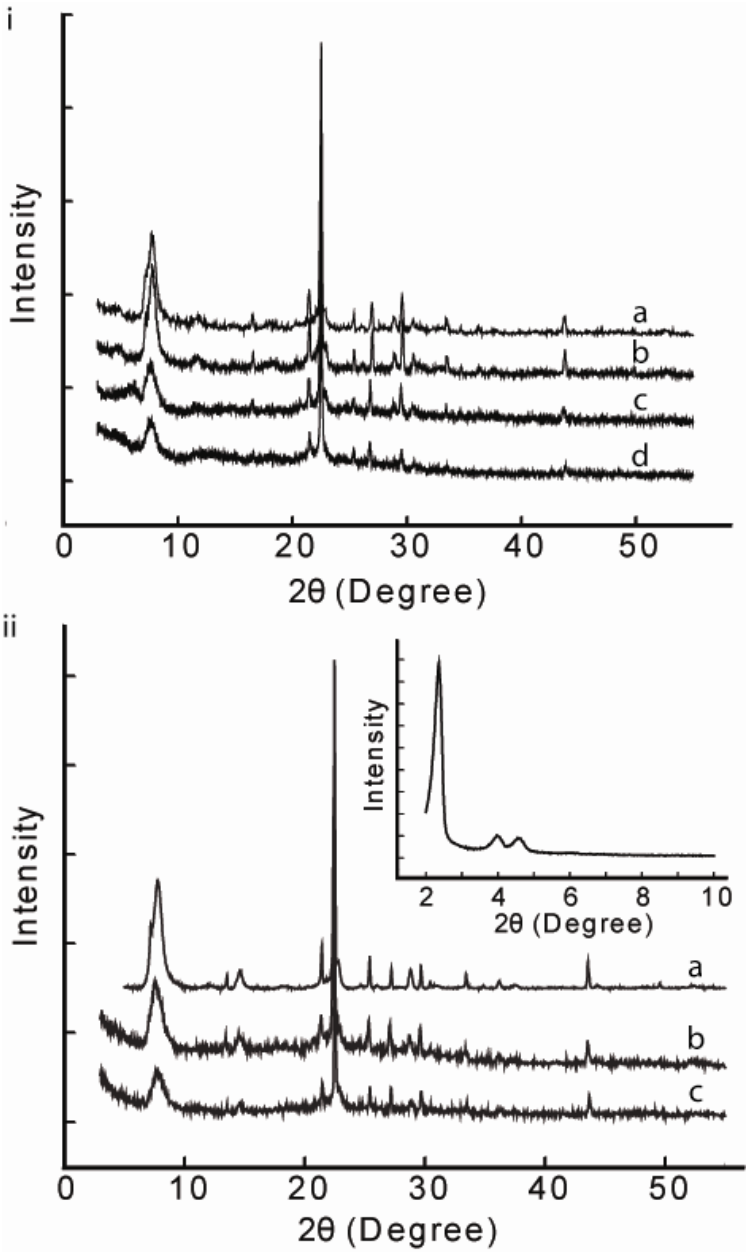

Figure S3. X-ray diffraction data from (i) as-synthesized samples. (a) Pure silica zeolite beta (PS-BEA), (b) PE functionalized pure silica zeolite beta (PE-PS-BEA), (c) PE-CIT-6, and (d) PE-BEA-100 (PE functionalized nanocrystalline beta synthesized from a gel with a SiO_2/Al_2O_3 = 100). (ii) sulfonated samples.(a) S-PE-PS-BEA, (b) S-PE-CIT-6, (c) S-PE-BEA-100. Inset shows S-PE-MCM-41 (sulfonated, PE grafted MCM-41).

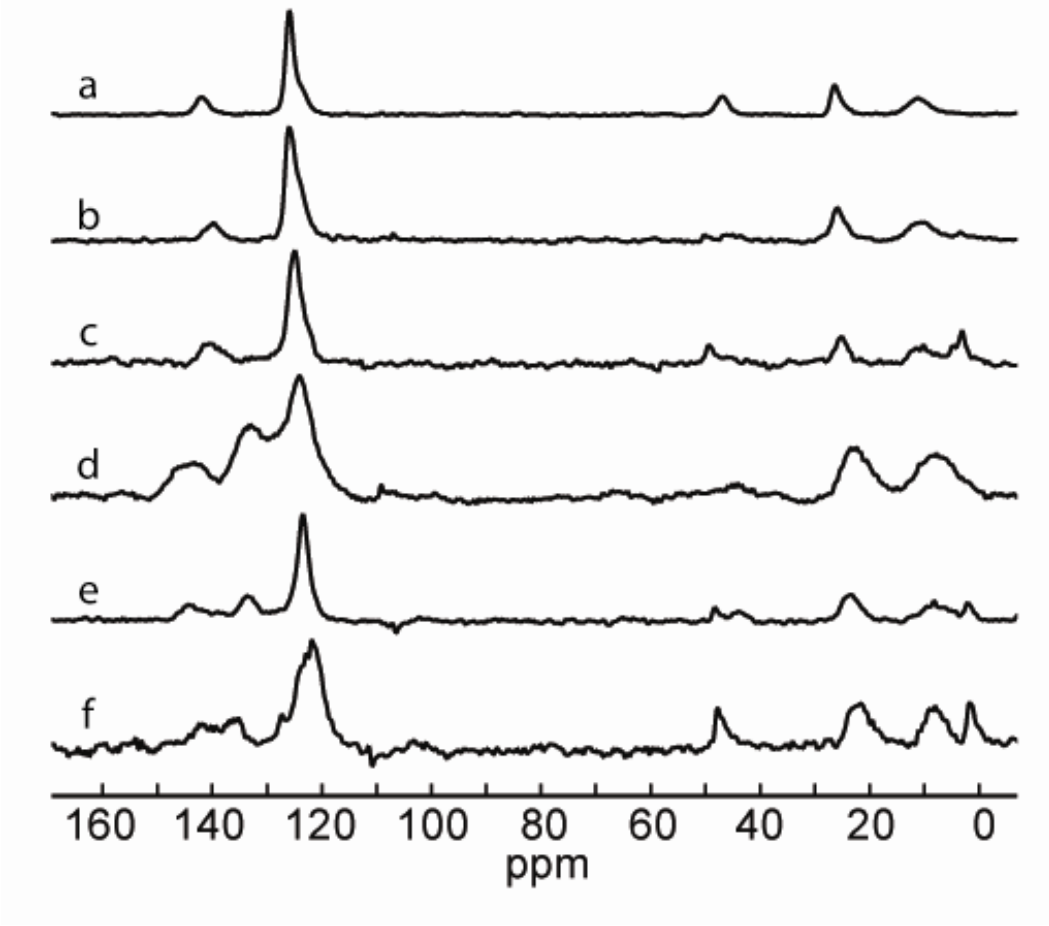

Figure S4. ^{13}C CPMAS NMR spectra of a. PE-MCM-41, b. acetic acid extracted PE-PS-BEA, c. acetic acid extracted (80 °C) PE-CIT-6, d. oleum treated (sulfonated) S-PE-MCM-41, e. oleum treated S-PE-PS-BEA, f. S-PE-CIT-6. Upon sulfonation, the aromatic peak at 140 ppm splits into two peaks 133 ppm and 145 ppm. The peak at 47 ppm in spectrum a. is a spinning side band. Residual TEA^+ peaks are evident at 1 ppm and 48 ppm in spectra b, c, e, and f.

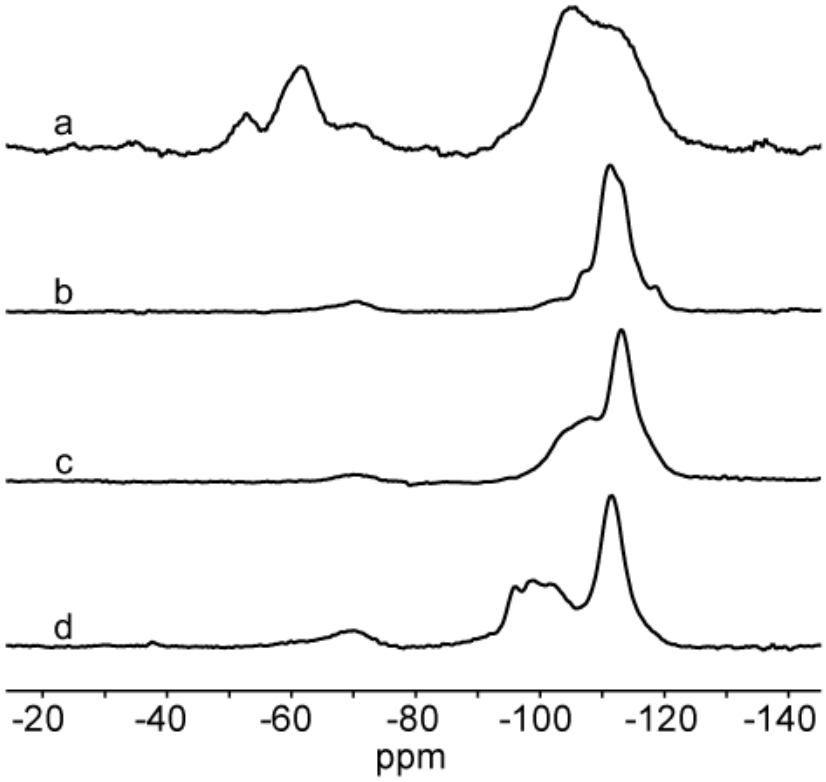

Figure S5. ^{29}Si CPMAS NMR spectra of a. PE-MCM-41, b. acetic acid extracted PE-PS-BEA, c. sulfuric acid extracted PE-BEA-100, and d. acetic acid extracted (80 °C) PE-CIT-6. T3 peaks are evident at -70 ppm in zeolite samples, while T3, T2, and T1 peaks appear in PE grafted MCM-41. Q peaks appear at more negative chemical shifts.

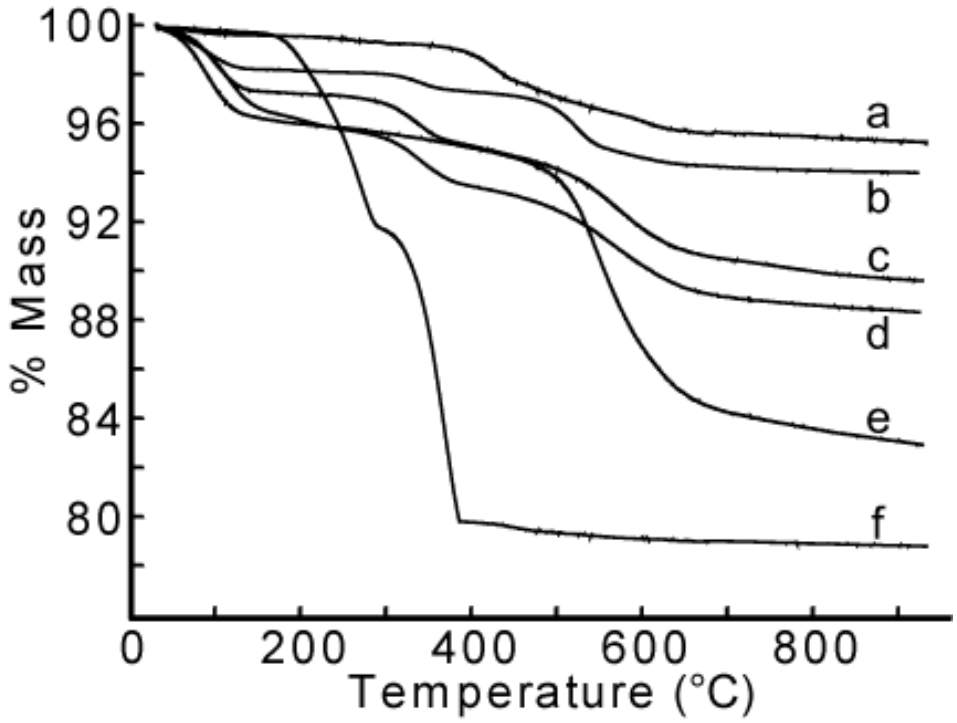

Figure S6. Thermogravimetric analysis traces of a. acetic acid extracted PE-PS-BEA, b. S-PE-PS-BEA, c. S-PE-CIT-6 (from 80 °C acetic acid extraction), d. S-PE-BEA-100, e. S-PE-MCM-41, f. as made PE-PS-BEA. Mass loss between 400-700 °C is attributed to combustion of the PE or S-PE groups. Mass loss under 200 °C is attributed to water and water bound to the sulfonic acid groups. The two mass losses in curve f. are attributed to the combustion of TEAOH and TEA^+. A small amount of tightly bound TEA^+ is observed in curves b., c., and d.

Sample Identity	Conductivity (RT/FH) (S/cm)
PE-PS-BEA	9.7E-05
PS-BEA	1.6E-04
BEA-50	1.9E-04
PE-BEA-50	1.7E-04
BEA-100	2.2E-04
PE-BEA-100	1.1E-04
BEA-400	1.8E-04
PE-BEA-400	4.8E-05

Table S1. Conductivity of as-made samples from gels with the indicated SiO_2/Al_2O_3 ratios. Typical SDA content is 20 wt. %.

(1) Camblor, M. A.; Corma, A.; Mifsud, A.; Perez-Pariente, J.; Valencia, S. *Studies in Surface Science and Catalysis* **1997**, *105*, 341.

(2) Holmberg, B. A.; Hwang, S.-J.; Davis, M. E.; Yan, Y. *Microporous and Mesoporous Materials* **2005**, *80*, 347-356.

(3) Jones, C. W.; Tsuji, K.; Davis, M. E. *Microporous and Mesoporous Materials* **1999**, *33*, 223-240.

(4) Camblor, M. A.; Corma, A.; Valencia, S. *Chemical Communications* **1996**, 2365.

(5) Takewaki, T.; Beck, L. W.; Davis, M. E. *Topics in Catalysis* **1999**, *9*, 35-42.

(6) Takewaki, T.; Beck, L. W.; Davis, M. E. *Journal of Physical Chemistry B.* **1999**, *103*, 2674-2679.